Monte Carlo Calculations of Solid-Fluid Equilibrium in Molecular Models of n-Alkane Mixtures

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The n-alkanes are archetypal systems for research in solid-fluid equilibrium for hydrocarbon systems and chain molecules in general. There are important features in the solid-fluid phase equilibrium, such as odd-even effects in the melting and triple point temperatures that provide macroscopic signature of the molecular scale behavior. Moreover they are important in the solid-fluid phase behavior in petroleum and natural gas processing. They also serve as important model systems for understanding the behavior of polymers and lipid biomembranes. Previous work in our group on single component n-alkanes has shown the importance of chain packing and molecular flexibility in determining the solid-fluid phase behavior. In this presentation we consider the extension of this work to mixtures. In particular we investigate the feasibility of calculating solid-fluid equilibrium for molecular models of n-alkane mixtures using Monte Carlo simulations.

Monte Carlo computer simulations have been used to study the solid-fluid phase equilibrium of a mixture of flexible hard sphere site united atom models of n-alkanes. We have considered a mixture representative of n-heptane/n-octane subject to an athermal torsional potential. As shown in previous work, this model gives qualitatively correct behavior for the structural effects on the pure components. To calculate the chemical potentials of the mixture from simulation required the development of a new methodology applicable to chain molecules. The fluid phase mixture properties were obtained by using the pure component properties and ideal solution theory. This approximation was tested at selected pressures and found to be accurate. Extensive calculations were done in the solid phase to calculate the chemical potentials and pressures of the model n-heptane/n-octane solid solution. The results together with the fluid phase properties were used to determine the phase diagram for the system. In the solid phase the system exhibits a eutectic point and solid phase miscibility is predicted only for systems rich in the longer chains.